PATENT SPECIFICATION

(11) 1365952

(21) Application No. 47521/71 (22) Filed 12 Oct. 1971

(31) Convention Application No. 30900 (32) Filed 13 Oct. 1970

(31) Convention Application No. 30901 (32) Filed 13 Oct. 1970 in

(33) Italy (IT)

(44) Complete Specification published 4 Sept. 1974

(51) International Classification C07C 103/06

(52) Index at acceptance

C2C 20Y 220 221 225 226 227 22Y 30Y 342 34Y 364 366 368 36Y 592 597 598 59X 602 63X KY

C3R 22D1A2 22D1AX 22D1B2 22D1BX 22D2A2 22D2AX 22D2B1 22D2BX 22M6 22N2 22P1 3D19 3D22 3D2A 3L6D

(19)

1365952

(72) Inventors LUIGI CICERI, FRANCESCO DI GREGORIO and EDOARDO PLATONE

SPECIFICATION NO 1365952 (47521/71)

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of ANIC S.p.A. an Italian Company, of Via M. Stabile 216, Palermo, Italy.

THE PATENT OFFICE R 78444/7

paring diesterdiamines which are useful as monomers in the synthesis of regular polyesteramides, and to the production of the polyesteramides.

Polyesteramides are known from the art having, in their macromolecule, characteristic units both of the type

$$\text{—COO—R—} \qquad (1)$$

and of the type

$$\text{C—O—NH—R—} \qquad (2)$$

where R is an aliphatic or aromatic radical.

Such compounds can be obtained in many ways, for example by polymerizing mixtures of diacids, diols and amines, or by starting from oxyacids and aminoacids, or by means of similar reactions. However, by employing such processes, the resulting polyesteramides have a structure wherein the units (1) and peated in a uniform and pre-established way. Such processes are based on the preliminary synthesis of complex monomers of the formula:

$$R^1OOC\text{—}R^2\text{—}CO\text{—}NH\text{—}R^3\text{—}NHCO\text{—}R^2\text{—}COOR^1$$

in which R^1 generally is a hydrogen atom or an alkyl radical having a low number of carbon atoms, e.g. methyl, R^2 is a divalent radical, preferably *p*-phenylene, and R^3 is a divalent radical of the type

$$\text{—}(CH_2)_n\text{—}$$

wherein n is a number ranging from 2 to 10.

In order to prepare such a complex monomer, two processes have so far been proposed; they are represented by the following schemes:

(a) $2\,R^1OOC\text{—}R^2\text{—}COCl + H_2N\text{—}R^3\text{—}NH_2 \rightarrow R^1OOC\text{—}R^2\text{—}CONH\text{—}R^3\text{—}NH\text{—}COR^2\text{—}COOR^1 + 2\,HCl$; and

(b) $2\,HOOC\text{—}R^2\text{—}COOH + H_2N\text{—}R^3\text{—}NH_2 \rightarrow HOOC\text{—}R^2\text{—}CONH\text{—}R^3\text{—}NH\text{—}COR^2\ COOH + 2\,H_2O$.

However, these processes have practical drawbacks; thus process (a) requires the preparation of expensive intermediates and a complicated synthesis, whereas process (b), although it is also very simple from a theoretical point of view, requires critical conditions because it is carried out via the formation of an intermediate salt showing two

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(19)

(72) Inventors LUIGI CICERI, FRANCESCO DI GREGORIO and EDOARDO PLATONE

(54) A PROCESS FOR PREPARING MONOMERS USEFUL TO THE SYNTHESIS OF REGULAR POLYESTER-AMIDES AND POLYESTER-AMIDES OBTAINED THEREBY

(71) We, SNAM PROGETTI S.p.A., an Italian Company, of Corso Venezia, 16, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for preparing diesterdiamines which are useful as monomers in the synthesis of regular polyesteramides, and to the production of the polyesteramides.

Polyesteramides are known from the art having, in their macromolecule, characteristic units both of the type

$$\text{—COO—R—} \qquad (1)$$

and of the type

$$\text{C—O—NH—R—} \qquad (2)$$

where R is an aliphatic or aromatic radical.

Such compounds can be obtained in many ways, for example by polymerizing mixtures of diacids, diols and amines, or by starting from oxyacids and aminoacids, or by means of similar reactions. However, by employing such processes, the resulting polyesteramides have a structure wherein the units (1) and (2) are arranged in an irregular way. Such an irregular structure adversely influences the mechanical properties of the product and, moreover, the characteristics of the products are difficult to reproduce.

Processes for obtaining polyesteramides having a regular structure have been proposed, wherein the units (1) and (2) are repeated in a uniform and pre-established way. Such processes are based on the preliminary synthesis of complex monomers of the formula:

$$R^1OOC\text{—}R^2\text{—}CO\text{—}NH\text{—}R^3\text{—}NHCO\text{—}R^2\text{—}COOR^1$$

in which R^1 generally is a hydrogen atom or an alkyl radical having a low number of carbon atoms, e.g. methyl, R^2 is a divalent radical, preferably *p*-phenylene, and R^3 is a divalent radical of the type

$$\text{—}(CH_2)_n\text{—}$$

wherein n is a number ranging from 2 to 10.

In order to prepare such a complex monomer, two processes have so far been proposed; they are represented by the following schemes:

(a) $2\,R^1OOC\text{—}R^2\text{—}COCl + H_2N\text{—}R^3\text{—}NH_2 \rightarrow R^1OOC\text{—}R^2\text{—}CONH\text{—}R^3\text{—}NH\text{—}COR^2\text{—}COOR^1 + 2\,HCl$; and

(b) $2\,HOOC\text{—}R^2\text{—}COOH + H_2N\text{—}R^3\text{—}NH_2 \rightarrow HOOC\text{—}R^2\text{—}CONH\text{—}\text{—}R^3\text{—}NH\text{—}COR^2\ COOH + 2\,H_2O$.

However, these processes have practical drawbacks; thus process (a) requires the preparation of expensive intermediates and a complicated synthesis, whereas process (b), although it is also very simple from a theoretical point of view, requires critical conditions because it is carried out via the formation of an intermediate salt showing two

quaternary ammonium atoms, and such a reaction is limited to a few kinds of diamines and particularly to those showing an aromatic nucleus in their molecule.

It is therefore an object of the present invention to provide a process for preparing the aforesaid complex monomers useful in the synthesis of regular polyesteramides and having a general appliance, which does not suffer from the drawbacks discussed above.

According to the present invention, there *is provided a process for preparing a diester-*diamide having the following general formula:—

$$R^4—O—\underset{\underset{O}{\|}}{C}—A—\underset{\underset{O}{\|}}{C}—NH—B—NH—\underset{\underset{O}{\|}}{C}—A—\underset{\underset{O}{\|}}{C}—O—R^4$$

wherein each R^4 is a hydrocarbon radical selected from acyclic alkyl radicals having from 1 to 8 carbon atoms, aryl radicals having from 6 to 10 carbon atoms, and cycloalkyl radicals having from 4 to 10 carbon atoms, with the proviso that when one radical R^4 is an aryl radical, the other radical R^4 is not an acyclic alkyl radical; and each of A and B; which may be the same or different, is an unsubstituted or substituted, aliphatic aromatic, divalent radical having from 2 to 30 carbon atoms, which process comprises reacting a dicarboxylic acid ester having the formula:

$$R^4—O—\underset{\underset{O}{\|}}{C}—A—\underset{\underset{O}{\|}}{C}—O—R^4$$

where R^4 and A are as defined above, with a diamine having the formula:

$$H_2N—B—NH_2$$

where B is as defined above, there being employed more than two moles of the dicarboxylic acid ester for each mole of said diamine.

The reaction can be regarded, for the sake of simplicity, as proceeding according to the following scheme:

$$2\,R^4—O—\underset{\underset{O}{\|}}{C}—A—\underset{\underset{O}{\|}}{C}—O—R^4 + H_2N—B—NH_2 \rightarrow$$

$$R^4—O—\overset{\overset{O}{\|}}{C}—A—\overset{\overset{O}{\|}}{C}—NH—B—NH—\overset{\overset{O}{\|}}{C}—A—\overset{\overset{O}{\|}}{C}—OR^4 + 2\,R^4OH \qquad (c)$$

The divalent hydrocarbon radicals A and B can be acyclic alkylene radicals for example:

$$—(CH_2)_m—,$$

$$—(CH_2)_m—\underset{\underset{CH_3}{|}}{CH}—,$$

$$—(CH_2)_m—\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{C}}—(CH_2)_m—,$$

$$—(CH_2)_m—\overset{\overset{CH_3}{|}}{CH}—\overset{\overset{CH_3}{|}}{CH}—(CH_2)_m—,$$

and

$$—\underset{\underset{CH_3}{|}}{CH}—(CH_2)_m—\overset{\overset{CH_2—CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}$$

in which m is an integer ranging from 2 to 20, providing that the total number of carbon atoms in the radical does not exceed 30; arylene radicals selected from, for example, p-phenylene, p-toluylene, p-xylylene, m-phenylene, m-toluylene and m-xylylene; or cycloalkylene radicals selected from, for example, 1,4-cyclohexylene, 1,3-cyclohexylene, 1,3-cycloamylene, 2 - methyl - 1,3 - cycloamylene, 2 - methyl - 1,4 - cyclohexylene, 2 - methyl - 1,3 - cyclohexylene, 1,3-cycloheptylene, 1,4-cycloheptylene and dicyclohexylmethylene.

The temperature at which the reaction is effected is not critical; however, it is advantageously selected in the range 20 to 250°C, depending on the employed working conditions. Preferably distillation is carried out during the reaction in order to remove the alcohol, R^4OH, so as to encourage the reaction.

As mentioned above, use is made of an excess of the diester; advantageously there are employed from 3 to 10 moles of diester per mole of diamine.

The reaction is usually carried out at atmospheric pressure and, in accordance with a preferred embodiment, under a stream of an inert gas. However, it can also be carried out under a reduced pressure.

Preferably the reaction is carried out at such a pressure and temperature as to keep the reactants in the liquid phase.

The reaction may be performed in the presence or absence of suitable solvents, for example aliphatic or aromatic hydrocarbons.

Although the reaction will proceed without employing a catalyst, it is advantageous to employ one of the usual compounds favouring trans-esterification reactions.

The following Examples illustrate different embodiments of the present invention, some of which embodiments are specifically referred to hereinabove.

Example 1

(Preparation of N,N′ - di(p - carbobutoxybenzoyl)dodecanediamine)

2780 g (10 moles) of di - (n - butyl) - terephthalate (obtained in a quantitative yield by trans-esterification between dimethylterephthalate and n-butanol) and 200.3 g (1 mole) of 1,12-diaminododecane were fed into a 5 litere four-necked flask provided with a stirrer, a nitrogen inlet, a distillation column and a thermometer positioned to be immersed in the reaction mixture. Under the atmosphere of nitrogen, the temperature of the reactants was in one hour increased to the range 200—210°C; after 3 hours, the temperature was raised so as to be in the range 220—225°C and maintained in that range for 1 hour.

About 100 ml of butyl alcohol were obtained as a secondary product (theoretical volume=165 ml). The reaction vessel was cooled to the range 130—140°C. The distillation column was replaced by a reflux condenser.

Then 2,000 cc of butyl alcohol were added, which cooled the suspension to 100°C. A filtration was then carried out using a filter funnel thermostatically maintained at a temperature of 100°C. A product precipitated from the filtered solution upon cooling: the product was recovered by further filtration, twice washed with 1500 cc of acetone and then dried at a temperature in the range 70—80°C.

The yield of this impure product was 598 g. It was purified by dissolving it in 7,500 cc of boiling n-butyl alcohol and filtering on a filter funnel externally heated at 100°C.

The oligomers present remained on the filter, and the monomer crystallized from the filtered butyl-alcohol upon cooling.

The yield was 432 g (71% with respect to the diamine); M.P.=167—168°C; free amine groups=8.6 eq/10^6 g; and elementary analysis: C=71.5% (theoretical 71.0); H=87% (theoretical=8.6); N=4.6% (theoretical=4.6).

Example 2

(Preparation of N,N′ - di(ω - carboethoxyvaleryl)ethylenediamine)

202 g (1 mole) of diethyladipate and 6.6 ml (0.1 mole) of ethylenediamine were fed to an apparatus similar to that described in Example 1. It was heated by increasing the temperature to 150°C over the course of one hour; and for 2 hours it was heated at a temperature ranging from 150 and 180°C, at the same time distilling the ethyl alcohol which was formed. The apparatus was cooled and the product was dispersed in 500 cc of diethyl ether; and solid was filtered, washed with another 500 of diethyl ether, and dried at 40°C. 32 Grams of raw product were obtained. The product was purified by heat extraction with 300 cc of benzene. Upon cooling the benzene solution, filtering the solid, washing the solid with 500 cc of benzene and drying, 16.2 g of the monomer were obtained in a yield of 43% with respect to the starting diamine. M.P.=121°C; C=57.5% (theoretical=58.0); H=8.6% (8.6); N=7.4 (7.5).

Example 3

(Preparation of N,N′ - di - (p - carbobutoxybenzoyl)hexamethylenediamine)

2780 g (10 moles) of dibutylterephthalate and 116 g (1 mole) of hexamethylenediamine were fed to a 5 litre flask provided with a mechanical stirrer, an immersed thermometer, a vigreux column and a distillation joint, the last two being as described in "Practical Organic Chemistry" by Arthur I. Vogel (3rd Edition).

Air was cooled by nitrogen and heating was begun, after one hour the temperature being raised up 200°C.

The reaction mass temperature was kept between 200 and 220°C for 4 hours, by distilling the butyl alcohol as it was produced.

Cooling was then effected, still in an inert atmosphere. When the temperature had fallen to about 150°C, 2,000 cc of butyl alcohol were continuously added, which cooled the suspension to 100°C. It was then filtered through a filter funnel thermostatically maintained at 100°C.

The product which precipitated from the filtered solution upon cooling was collected by filtering, washed four times with 2 litres of acetone, and dried under vacuum at 60°C. 460 g of raw product were obtained. The monomer was purified by being dissolved in boiling *n*-butyl alcohol, and being heat filtered. 328 g of monomer were obtained upon cooling the *n*-butyl alcohol solution: yield= 62.5% with respect to the starting diamine: M.P.=187°C, free amine groups=10.6 eq/10^6 g; C=68.9% (theoretical=68.8); H=7.6 (7.6); N=5.1 (5.34).

Example 4

(Preparation of N,N' - di(*p* - carbopropoxybenzoyl)hexamethylenediamine)

500 g (2 moles) of dipropylterephthalate and 23.2 g (0.2 moles) of hexamethylenediamine were fed to an apparatus similar to that of Example 3. The apparatus was heated to 200°C over the course of 45 minutes, and was kept at 220°C for 4 hours, by distilling off the propyl alcohol as it was formed. The apparatus was cooled and the mass was recovered by dispersing it in 1 l of acetone; the dispersion was filtered and the solid material was washed with another 600 cc of acetone and then dried in a stove.

The product was purified by extracting it with hot *n*-propyl alcohol in a Kumagawa extractor. The purified product had a M.P.= 193—194°C; yield=50% with respect to the starting diamine. Free amine groups=28 equiv/10^6 g.

Example 5

(Preparation of N,N' - di(*p* - carbobutoxybenzoyl)ethylenediamine)

278 g of *n*-butylterephthalate and 6.6 ml of ethylenediamine were refluxed for 2 hours at 200°C and at room pressure; then the volatile part (i.e. alcohol produced during the reaction) was distilled for 2 hours again at 200°C. The resulting mass was cooled to about 150°C, and 500 c of *n*-BuOH were continuously added. The mixture was allowed to stand for one night. It was then filtered and the solid recovered: it was washed with 150 cc of BuOH and dried; 34 g of product were obtained, which were purified by heat extraction with 500 cc of *n*-BuOH. The monomer was extracted, while the oligomers remained undissolved. By cooling the butyl alcohol solution, 22 g of product were obtained: M.P.=210—212°C. Elementary analysis: C=66.8 (theoretical=66.6); H=7.1 (6.83); N=5.6 (5.97).

Example 6

(Preparation of N,N' - di(ω - carboethoxyvaleryl)dodecamethylenediamine).

20 g of dodecamethylene - 1,12 - diamine and 202 g of diethyladipate were fed to a three-necked 500 cc flask provided with a mechanical stirrer, immersed thermometer and distillation column. The atmosphere was kept inert, and the temperature was raised to 152°C and maintained there for 3 hours. Then the temperature was increased to 170°C and the heating continued for 3 hours. The ethyl alcohol formed by the reaction was distilled off. At the end of the reaction, the mass was cooled and allowed to stand for a night; the resulting semi-solid mass was recovered with 250 cc of diethyl ether. It was filtered and washed three times with 100 cc of diethyl ether. The resulting solid (57 g) was purified by heat extraction with benzene for 3 hours.

The monomer crystallized from the benzene solution upon cooling; it was filtered, washed with 100 cc of diethyl ether and dried; 34 g were obtained of a product having a melting point in the range 116—119°C. Elementary analysis: C=65.7 (theoretical=65.6); H=10.2 (10.1); N=5.7 (5.4).

Example 7

(Preparation of N,N - di(ω - carboethoxyvaleryl) - 4,4' - diaminodiacyclohexylmethane)

202 g of diethyladipate and 21 g of 4,4'-diaminodicyclohexylmethane were reacted in an inert atmosphere at 160°C for 4 hours and at 170°C for 1 hour. The ethyl alcohol which formed was distilled off. The reaction product was cooled and the semi-solid mass was recovered with 200 cc of diethyl ether, filtered and washed three times with 100 cc aliquots of diethyl ether. The raw product was purified by heat extraction with 900 cc of benzene. The monomer crystallized out upon cooling the benzene solution. After being filtered and washed with 100 cc of benzene and then with 200 cc of diethyl ether, the product weighed 17.3 g: M.P.=200—205°C. Elementary analysis: C=67.1 (theoretical=66.7); H=9.8 (0.57); N=5.6 (5.36).

Example 8

(Preparation of N,N' - di(*p* - carbobutoxybenzoyl) - meta - xylylene - diamine)

278 g of *n*-butylterephthalate and 13.6 g of *m*-xylylenediamine were fed to a three-necked 500 cc flask provided with a mechanical stirrer, plunger, thermometer and stripping little column. The atmosphere in the flask was kept inert and the flask was heated at 200°C for 6 hours. It was then slowly cooled to 80°C, then 200 cc of benzene were added, and the resulting mixture was allowed to stand

for one night. The white precipitate which formed was recovered by filtration and washed three times with cold benzene (50 cc each time); then it was dried and 60.8 g were obtained. 10 g of the obtained product were purified by heat extraction with benzene (200 ml) for three hours. The monomer crystallized from the hot benzene solution upon cooling; it was filtered, washed with 30 cc of cold benzene and then weighed (5.2 g). M.P.=143—144°C. Elementary analysis: C=70.1 (70.6); H=6.8 (6.6); N=4.9 (5.15).

Example 9

(Preparation of N,N′ - di(*p* - carbomethoxybenzoyl)hexamethylenediamine)

305 g (1.57 moles) of dimethylterephthalate, 18.2 g (0.157 mole) of 1,6-hexamethylenediamine, 1084 cm^3 of anhydrous toluene, 361 cm^3 of absolute methyl alcohol and 40 cc of a 1.23 *M* solution in methyl alcohol of $CH_3O^-Li^+$ were fed to a 3 litre flask provided with a reflux condenser, mechanical stirrer and nitrogen inlet.

The mass was stirred during reflux heating. From an initially clear solution, after 1.5 hours of refluxing a reaction product began to separate. The heating was continued for a further 6.5 hours and then the mixture was filtered at a temperature of 65°C; the solid obtained was dispersed in 200 cc of toluene at 65°C, and then filtered; this last step was repeated. The product was then washed twice with 200 cc of boiling methyl alcohol. The product, dried in a stove, weighed 64.2 g (93.8% yield calculated with respect to the diamine) and could be polymerized without further purification. M.P.=233—236°C. C=65.7 (65.5); H=6.6 (6.36); N=6.6 (6.36).

Example 10

(Preparation of N,N′ - di(*p* - carbomethoxybenzoyl)dodecamethylenediamine)

40.04 Grams (0.2 mole) of 1,12-dodecamethylene diamine in 1,456 cm^3 of anhydrous toluene, and 484 cc of absolute methyl alcohol containing 0.063 mole of CH_3OLi were reacted in an apparatus similar to that of Example 9, with 388 g (2 moles) of dimethylterephthalate.

The resulting mixture was refluxed and, from an initially clear solution, after about 1.5 hours of refluxing there began to separate the desired product.

The refluxing was continued for another 8.5 hours, then the mixture was filtered at 65°C, the solid was washed twice with 200 cc aliquots of toluene at 65°C and then washed twice with boiling methyl alcohol (200 cc each time). The solid was dried in a stove and the dried product could directly be used in polymerization without further purification; it had the following characteristics: M.P.=203—205°C; C=68.8 (68.7); H=7.82 (7.64); N=5.45 (5.34).

Example 11

(Preparation of N,N′ - di(*p* - carbomethoxybenzoyl)dodecamethylenediamine)

1940 Grams (10 moles) of dimethylterephthalate and 400.4 g (2 moles) of 1,12-dodecanediamine were dissolved in 6.4 l of anhydrous toluene and 1.6 l of absolute methyl alcohol in an apparatus similar to that of Example 9. 188 cc of a 1.41 *M* solution in methyl alcohol of CH_3OLi were added. The mixture was refluxed.

N,N′ - di(*p* - carbomethoxybenzoyl)dodecamethylenediamine was removed from the initially clear solution, after 0.5 hour of refluxing. The heating was continued for 6.5 hours, then the mixture was filtered at 65°C and the solid was washed twice with 3 litre aliquots of hot toluene (65°C) and twice with 5 litre aliquots of boiling methyl alcohol. After drying it in a stove, the product weighed 981 g (93.5% yield with respect to the diameter compound). M.P.=203—205° C.

Example 12

(Preparation of N,N - di(*p* - carbomethoxybenzoyl)dodecamethylenediamine)

In an apparatus similar to that of Example 9, in an inert atmosphere, 116.4 g (0.6 mole) of dimethylterephthalate were reacted, under stirring and reflux heating, with 40.04 g (0.2 mole) of 1,12-dodecamethylenediamine dissolved in 645 cm^3 of anhydrous toluene and 162 cm^3 of methyl alcohol, to which were added 185 cm^3 of an 1.41 *M* solution in methyl alcohol of CH_3OLi. N,N - di(*p* - carbomethoxybenzoyl)dodecamethylenediamine began to precipitate from the initially clear solution after about 0.5 hour of boiling. The heating was continued for 6.5 hours, then the mixture was heat filtered at 65°C; the solid was washed twice with 200 cc aliquots of toluene at 65°C and twice with 200 cc aliquots of boiling methyl alcohol. After drying in a stove, the product weighed 84 g (80% with respect to diamine) and had a melting point of 202—204°C.

Example 13

(Preparation of a polyesteramide from N,N′ - di(*p* - carbobutoxybenzoyl)dodecamethylenediamine and dodecan - 1,12 - diol (12 N T 12))

262 Grams (0.43 mole) of N,N′ - di - (*p* - carbobutoxybenzoyl) dodecamethylenediamine, obtained according to Example 1, were introduced into a 1,000 cc flask provided with a vacuum stirrer, an inlet for inert gas and a Vigreux column having a distillation joint.

The diamine was gas freed under vacuum for 1 hour, and then, in an inert atmosphere, were added 217 g (1.075 mole) of dodecan - 1,12 - diol and 0.43 cc of a 0.2 *M* solution in butyl alcohol of tetrabutyl titanium. The flask was immersed into a bath maintained at

200°C and stirred, always in inert atmosphere, at this temperature for 180 minutes, and then for 205 minutes at 220°C. 77 cc of butyl alcohol were recovered. The Vigreux column was replaced by a short distillation joint; it was joined to the vacuum inlet and, over 100 minutes, the pressure was reduced from 760 to 0.5 mmHg, while the temperature of the heating medium was increased from 220 to 260°C. Then, keeping the pressure constant, the temperature was raised to 270°C and, after 55 minutes, the polycondensation was stopped. A polymer was obtained which was substantially uncoloured and which had a relative viscosity of 2.52, measured at 25°C in a phenol-tetrachloroethane solution (50:50), at a concentration of 1 g/dl. The polymer, of which the density was 1.160, was, by means of a known technique, extruded as a single filament by a melting-spinning apparatus at the temperature of 280°C and then drawn, the pin and plate being at the temperatures of 30 and 150°C, respectively. The drawn filament was dyed at 100°C using a type CI Dispersed Orange 13 dye, in a large excess (>100%) at a buffered pH of 5.5 [$(NH_4)_2SO_4$+H COOH] and a ratio of dye:solution in the bath of 1:100. From the saturation isotherm were obtained the rate dyeing constant and the value of the saturation concentration. In the following Table 1 there are reported the values of the obtained mechanical and dyeing characteristics.

TABLE 1

Filament as such	count (den)	10.7
	toughness (g/den)	5.1
	elongation %	15
	modulus (g/den)	60
	wet modulus / dry modulus %	97
Dyeability	K_{100} g^2/Kg^2 sec	15.3
	C_∞ %	40.5
Filament after having been boiled in water for 20 minutes	toughness (g/den)	4.5
	elongation %	22
	modulus (g/den)	40
	wet modulus / dry modulus %	100
Filament treated in air for 10 minutes at 160°C and then boiled for 30 minutes in water	toughness (g/den)	4.6
	elongation %	20
	modulus (g/den)	42
	wet modulus / dry modulus %	90

Example 14

(Preparation of N,N' - di(p - carbomethoxybenzoyl) m-xylylenediamine)

960 cc of anhydrous toluene, 210 cc of pure methyl alcohol, 40.8 g (0.3 mole) of m-xylylenediamine and 407.8 g of dimethylterephthalate (2.1 moles) were put into a 3 litre three-necked flask provided with a stirrer, a reflux condenser and an inert gas inlet. Then the mixture was brought thermostatically to 67—70°C and to it were added 65.2 cc of a 0.83 M solution in methyl alcohol of CH_3OLi. A precipitate formed after 70 minutes and the reaction could be regarded as being finished after seven hours.

The product was separated by hot filtration, washed with toluene to remove the excess of dimethylterephthalate and then with water at 60°C to remove the catalyst. The white solid weighing 112 g, upon differential thermal analysis, showed a m.p. of 213°C; it had a content of amine groups equal to 28.2 meq/kg and the following elementary analysis:

	C	H	N
calculated	67.80	5.20	6.10
found	68.00	5.30	6.20

Example 15

(Preparation of N,N' - di(p - carbomethoxybenzoyl) - 1,4 - di(aminomethyl)cyclohexane)

In an apparatus similar to that described in Example 14, 407.4 g of dimethylterephthalate and 42.6 g of 1,4-di(aminomethyl)-cyclohexane were dissolved in 960 cc of anhydrous toluene and 235 cc of pure methyl alcohol.

The resulting mixture was heated at a temperature in the range 67—70°C and then to it were added 49.4 cc of 1.21 M solution in methyl alcohol of CH_3OLi. The reaction was completed after 9 hours. The product which precipitated was hot filtered on a lined Buchner filter, washed with 1 l of hot toluene and then with hot water to remove the catalyst. The white solid, obtained in a yield of 79% with respect to the starting diamine, had a melting point of 278°C, a content of amine groups equal to 41.3 meq/kg and the following elementary analysis:

	C	H	N
calculated	66.90	6.44	6.01
found	66.80	6.70	6.30

Example 16

(Preparation of N,N' - di(p - carbomethoxybenzoyl) - 1,2 - diaminoethane)

Using the same apparatus as Example 1, 12 g of 1,2 diaminoethane were reacted with 233 g of dimethylterephthalate dissolved in 650 cc of boiling toluene and 170 cc of boiling methyl alcohol. 14.4 cc of a 1.91 M solu-

tion in methanol of CH_3OLi were added. The reaction was stopped after 5 hours. The product was hot filtered on a lined Buchner filter, washed with 500 cc of hot toluene (70°C) and then with 500 cc of cold water to remove the catalyst.

The resulting white solid (25 g) was recrystallized from dimethylformamide at 80° C. It had a m.p. of 315°C, and a content of amino groups equal to 28.6 meq./kg. The elementary analysis was performed on $C_{20}H_{20}H_2O_6$:

	C	H	N
calculated	62.6	5.4	7.3
found	62.7	5.4	7.5

Example 17

(Preparation of N,N′ - di(ω - carbomethoxycapryloyl) - 1,12 - dodecanediamine)

Employing an apparatus similar to that described in Example 14, 40 g of 1,12-dodecanediamine were dissolved in 650 cc of anhydrous toluene and 158 cc of anhydrous methyl alcohol. After having added 260 g of dimethylazelate, the mixture was heated to achieve complete dissolution (70°C). Then 14.4 cc of a 1.91 *M* solution in methyl alcohol of CH_3OLi were added.

The reaction was continued for 9 hours. The product was cooled and filtered on a Buchner filter. The precipitate was cold washed with 500 cc of diethyl ether. 81 Grams of product was recrystallized from boiling methyl alcohol, using 50 cc of alcohol per gram of product. The white solid, obtained in a yield of 71% with respect to the initial diamine, had a melting point of 129° C, calculated by differential thermal analysis, and a content of free amine groups equal to 44.6 meq/kg. The elementary analysis for $C_{32}H_{60}N_2O_6$ was the following:

	C	H	N
calculated	67.6	10.57	4.93
found	67.8	10.7	5.3

Example 18

(Preparation of N,N′ - (di(*p* - carbomethoxybenzoyl) - 1,7 - heptanediamine)

Making use of the same apparatus as used in Example 14, 26 g of 1,7-heptanediamine were dissolved in 780 cc of anhydrous toluene and 220 cc of methyl alcohol. 233 Grams of dimethylterephthalate were added to the mixture and the resulting mixture was heated up to complete dissolution. Then 17.3 cc of a 1.91 *M* solution in methyl alcohol of CH_3OLi were introduced. After 60 minutes the diamidoester compound began to precipitate. The reaction was continued under stirring for 270 minutes. The reaction product was cooled to room temperature and 2 l of chloroform were added to dissolve the unreacted dimethylterephthalate. The residual product was filtered and dried under high vacuum. The white solid (93 g) was further washed with boiling chloroform, and then with cold methyl alcohol to remove all traces of the catalyst. The resulting diesterdiamide had a yield of 57% with respect to the diamine, had a melting point of 220°C, calculated by means of differential thermal analysis, had a content of free amine groups equal to 39.2 meq/kg and had the following elementary analysis ($C_{25}H_{30}N_2O_6$):—

	C	H	N
calculated	66.10	6.61	6.17
found	66.50	7.0	6.53

Example 19

(Preparation of N,N - di(*p* - carbomethoxybenzoyl - 1,5 - diaminopentane)

Working according to Example 18, 24.5 g of 1,5 - pentamethylenediamine and 233 g of dimethylterephthalate were hot-dissolved in a mixture consisting of 780 cc of anhydrous toluene and 220 cc of methyl alcohol.

When the suspension became clear, 17.3 cc of a 1.91 *M* solution in methyl alcohol of CH_3OLi were added. A precipitate was formed after 65 minutes. The reaction was continued under stirring for 270 minutes. The diamidodiester compound was hot filtered on a lined Buchner filter and washed with 1 l of hot chloroform to remove the excess of dimethylterephthalate. After cooling, the product was filtered and washed with hot methyl alcohol to remove all traces of the inorganic salt. The resulting white solid weighed 61 g (yield of 59.6% with respect to the charged diamine); it was recrystallized from dimethylformamide at 90—100°C. On differential thermal analysis it showed a m.p. of 229°C. The content of free amine groups was 29.3 meq/kg and the elementary analysis for $C_{23}H_{26}N_2O_6$ agreed with the theoretical composition.

Example 20

(Preparation of N,N - di(ω - carbomethoxycapryloyl)*m*-xylylenediamine)

Making use of the apparatus of Example 14, 28 g of *m*-xylylenediamine and 250 g of dimethylazelate were hot dissolved in a mixture consisting of 390 cc of anhydrous toluene and 110 cc of methyl alcohol. Then 17.3 cc of a 1.91 *M* solution in methyl alcohol of CH_3OLi were added. The reaction was continued at 67—70°C for 300 minutes and then 1500 cc of a mixture constituted by heptane and diethyl ether (1:1) were added in order to precipitate the diamidodiester. The separated product was filtered on a Buchner filter, repeatedly washed with the same mixture of solvents and then with water to remove the catalyst.

The dried product weighed 40 g. The differential thermal analysis showed a melt-

ing point of 113°C, and the elementary analysis showed the following composition (for $C_{28}H_{44}N_2O_6$):—

	C	H	N
calculated	66.7	8.73	5.56
found	66.8	8.70	5.60

Example 21

(Preparation of N,N′ - di(*p* - carbobutoxybenzoyl) - 1,12 - dodecanediamine)

Working according to Example 20, 40 g of 1,12-dodecanediamine and 334 g of dibutylterephthalate were mixed with 650 cc of anhydrous *n*-heptane and 170 cc of *n*-butyl alcohol. The mixture was heated at 95°C and, when the solution was clear, 14.5 cc of a 1.17 *M* solution in methyl alcohol of *n*-C_4H_9OLi were added. The diamidodiester almost instantaneously precipitated. The reaction could be thought as being finished after 70 minutes. The product was filtered at 70°C, washed with acetone and recrystallized from boiling *n*-butyl alcohol. The white solid had a melting point in the range 166—168°C and a content of free amine groups of 29.4 meq./kg. The elementary analysis approximately agreed with theoretical composition:

	C	H	N
calculated	71.0	8.6	4.6
found	71.3	8.7	4.6

Example 22

(Preparation of N,N′ - di(*p* - carbobutoxybenzoyl) - 1,12 - dodecamethylenediamine)

A reaction was performed between dibutylterephthalate (DBT) and dodecamethylenediamine (DMDA) in a xylene-butyl alcohol mixture.

DBT	166.8 g	(0.6 mole)
DMDA	20 g	(0.1 mole)
MeONa	0.54 g	(0.01 mole)
Xyl/butyl alcohol 75/25		400 ml

Use was made of a 1 l three-necked flask provided with a reflux condenser, a stirrer and a nitrogen inlet. The flask was flushed out with nitrogen, then DBT was dissolved in the solvent and heated. The catalyst (MeONa) and the diamine were added, and the reaction was continued with boiling for 7 hours. To the reaction mixture was added 1 l of acetone in order to facilitate the filtration; at the end the product was washed with acetone and then with diethyl ether. It was then dried in a stove under vacuum at 70°C. The product had a melting point of 171°C; the elementary analysis was:

	C	H	N
calculated	71.05	8.55	4.60
found	70.8	8.55	4.65

20 g of product were obtained, corresponding to a 33% yield.

Example 23

(Preparation of N,N′ - di(*p* - carbomethoxybenzoyl) - 1,12 - dodecanediamine)

388 Grams (2 moles) of dimethylterephthalate, 80 g of 1,12-dodecanediamine, 1280 cc of anhydrous toluene, 320 cc of absolute methyl alcohol and 37.6 cc of a 1.41 *M* solution in methyl alcohol of CH_3OLi were introduced into a 3 l autoclave provided with an efficient stirrer, the whole operation being carried out under an inert atmosphere. As soon as the autoclave had been shut, the reaction vessel was washed with a nitrogen stream (by alternating a vacuum with a nitrogen atmosphere). The heating was performed until a temperature of 130°C was reached. The pressure increased to about 9 Kg/cm².

The reaction ended after two hours. The mixture was discharged from the autoclave, hot filtered (65°C) and the solid washed twice with 600 cc of hot toluene and twice with 1 l of boiling methyl alcohol. The product was dried in a stove, and it weighed 190 g; the yield was 90.9% with respect to the starting diamine. M.P.=203—20.5°C; free amine groups content=55 meq/Kg; elementary analysis agreed with the theoretical composition.

Example 24

(Preparation of N - N′ - di(*p* - carbomethoxybenzoyl) - 4,4′ - diaminodiphenylether)

At the temperature of 67—70° and working in an apparatus similar to that of Example 14, 116.4 g of dimethylterephthalate were dissolved in 400 c of a toluenemethyl alcohol mixture (72:25 by volume). 10.8 Grams of sodium methylate and 20 g of 4,4′ diaminodiphenylether were then added. A grey and barely-perceptible dispersion was formed. Under a nitrogen atmosphere the mixture was heated up to boiling for 10 hours. At the end it was cold treated with HCl in a stoichiometric amount with respect to the catalyst and was stirred for some time. Then the solid was filtered, and repeatedly washed with chloroform to remove the excess of dimethylterephthalate and then washed with methyl alcohol. The white solid, obtained in a yield (with respect to the starting diamine) of 38% had a m.p. of 341°C and the following elementary analysis:

	C	H	N
found	68.2	4.6	5.2
calculated	68.7	4.5	5.3

The present invention also includes polyesteramides obtained by polycondensing diesterdiamides of the present invention.

WHAT WE CLAIM IS:—

1. A process for preparing a diesterdiamide having the following general formula:—

$$R^4{-}O{-}\underset{\underset{O}{\|}}{C}{-}A{-}\underset{\underset{O}{\|}}{C}{-}NH{-}B{-}NH{-}\underset{\underset{O}{\|}}{C}{-}A{-}\underset{\underset{O}{\|}}{C}{-}O{-}R^4$$

wherein each R^4 is a hydrocarbon radical selected from acyclic alkyl radicals having from 1 to 8 carbon atoms, aryl radicals having from 6 to 10 carbon atoms, and cycloalkyl radicals having from 4 to 10 carbon atoms, with the proviso that, when one radical R^4 is an aryl radical, the other radical R^4 is not an acyclic alkyl radical; and each of A and B, which may be the same or different, is an unsubstituted or substituted, aliphatic or aromatic, divalent radical having from 2 to 30 carbon atoms, which process comprises reacting a dicarboxylic acid ester having the formula:

$$R^4{-}O{-}\underset{\underset{O}{\|}}{C}{-}A{-}\underset{\underset{O}{\|}}{C}{-}O{-}R^4$$

where R^4 and A are as defined above, with a diamine having the formula:

$$H_2N{-}B{-}NH_2$$

where B is as defined above, there being employed more than two moles of the dicarboxylic acid ester for each mole of said diamine.

2. A process according to Claim 1, wherein the radicals A and/or the radical B is/are selected from:

$$-(CH_2)_m-,$$

$$-(CH_2)_m-\underset{\underset{CH_3}{|}}{CH}-,$$

$$-(CH_2)_m-\overset{\overset{CH_3}{|}}{\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{C}}-(CH_2)_m-,$$

$$-(CH_2)_m-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-(CH_2)_m-,$$

and

$$-\underset{\underset{CH_3}{|}}{CH}-(CH_2)_m-\overset{\overset{CH_2-CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}$$

in which m is an integer ranging from 2 to 20, providing that the total number of carbon atoms in the radical does not exceed 30.

3. A process according to Claim 1 or 2, wherein the radicals A and/or the radical B is/are selected from *p*-phenylene, *p*-toluylene, *p*-xylylene, *m*-phenylene, *m*-toluylene, *m*-xylylene, 1,4-cyclohexylene, 1,3-cyclohexylene, 1,3-cycloamylene, 2 - methyl - 1,3 - cycloamylene, 2 - methyl - 1,4 - cyclohexylene, 2 - methyl - 1,3 - cyclohexylene, 1,3-cycloheptylene, 1,4-cycloheptylene and dicyclohexylmethylene.

4. A process according to Claim 1, 2 or 3, wherein there are employed from 3 to 10 moles of the dicarboxylic acid ester per mole of said diamine.

5. A process according to any preceding claim, wherein the reaction is carried out in an inert gas atmosphere.

6. A process according to any preceding claim, wherein the reaction is carried out at atmospheric pressure.

7. A process according to any one of Claims 1 to 5, wherein the reaction is carried out at a pressure lower than atmospheric pressure.

8. A process according to any one of Claims 1 to 5, wherein the reaction is carried out at such a pressure and temperature as to keep reactants in the liquid phase.

9. A process according to any preceding claim, wherein the reaction is carried out in the presence of an organic solvent.

10. A process according to Claim 9, wherein the solvent is an aliphatic or aromatic hydrocarbon.

11. A process according to any preceding claim, wherein the reaction is carried out at a temperature in the range from 20 to 250°C.

12. A process for preparing a diesterdiamide, substantially as described in any one of the foregoing Examples 1 to 12.

13. A process for preparing a diesterdiamide, substantially as described in any one of the foregoing Examples 14 to 24.

14. A diesterdiamide having the formula defined in Claim 1, whenever obtained according to the process claimed in any preceding claim.

15. Process for preparing a polyesteramide, which comprises polycondensing a diesterdi-

amide as defined in Claim 1 and as claimed in Claim 14.

16. A process for preparing a polyesteramide, substantially as described in the foregoing Example 13.

17. A polyesteramide whenever obtained by a process according to Claim 15 or 16.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
28, Southampton Buildings,
Chancery Lane,
London, WC2A 1AT.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.